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5

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10 (54) Method for treating a cobalt-based heat resistant alloy

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SPECIFICATION

1. Title of the invention

25 Method for treating a cobalt-based heat resistant alloy

2. Claims

Method for treating a cobalt-based heat resistant alloy characterized in that a cobalt-based heat resistant alloy comprising, as wt%, Cr: 10-35%, Ni: 0-30%, W: 0-25%, Mo: 0-10%, C: 0.01-1.0%, Zr: 0-1.0%, B: 0-1.0%, Fe: 0-8%, Ti: 0-2%, Al: 0-2%, Nb: 0-5%, Ta: 0-10%, Y: 0-1.0%, Co: remainder, is subjected to chromizing treatment with simultaneous solution heat treatment of the alloy at 1050-1200°C, and then
35 subjected to ageing treatment at no more than 1000°C.

3. Detailed description of the invention

The present invention relates to an improved method for carrying out efficient heat treatment such as chromizing on cobalt (Co)-based heat resistant alloy products.

Chromizing treatment or other surface treatment is often carried out on products made by using Co-based heat resistant alloys, such as static blades for gas turbines and jet engines, and high temperature components of chemical engineering equipment, for example, especially in order to improve high-temperature corrosion resistance; however, when carrying out chromizing treatment on Co-based heat resistant alloy products, methods such as the following are ordinarily adopted. Namely, carrying out heat treatment comprising chromizing treatment by holding for several hours to tens of hours at around 900-1200°C and then cooling, followed by solution heat treatment by holding for 1-5 hours at 1100-1200°C in a non-oxidizing atmosphere then cooling to an ageing temperature of 900-1000°C, followed by ageing treatment by holding for several hours to tens of hours at 900-1000°C, and then cold hearth, air cooling or quenching. As indicated above, if solution heat treatment after chromizing treatment is carried out in the atmosphere, the chromizing treatment layer is oxidized and is lost, so that there is essentially no benefit from chromizing treatment. Therefore, solution heat treatment needs to be carried out in a non-oxidizing atmosphere, so that a special heat treatment furnace is necessary, and it is also uneconomic in terms of time and heat energy.

As the result of concerted studies intended to discover an economic and easy method for heat treatment, including chromizing treatment, in order to obtain an adequate chromizing treatment layer thickness without detracting from the mechanical properties and metal structure of Co-based heat resistant alloys, the present inventor has discovered the following. Thus,

the present invention has been perfected based on the discovery that as regards Co-based heat resistant alloys, by setting an adequate time at a temperature of 1050-1200°C, considering solid solution of the alloy and chromizing treatment layer thickness, it is possible to carry out chromizing treatment and solution heat treatment of the alloy at the same time. Thus, the present invention relates to a method for treating a cobalt-based heat resistant alloy characterized in that a cobalt-based heat resistant alloy comprising, as wt%, Cr: 10-35%, Ni: 0-30%, W: 0-25%, Mo: 0-10%, C: 0.01-1.0%, Zr: 0-1.0%, B: 0-1.0%, Fe: 0-8%, Ti: 0-2%, Al: 0-2%, Nb: 0-5%, Ta: 0-10%, Y: 0-1.0%, Co: remainder, is subjected to simultaneous chromizing and solution heat treatment of the alloy at 1050-1200°C, and then subjected to ageing treatment at no more than 1000°C.

In the present invention the time necessary for adequate solid solution, of the alloy and chromizing treatment layer thickness is 3-15 hours, and the subsequent ageing treatment should be carried out at a temperature of no more than 1000°C; thus, after slow cooling, for example, to 900-1000°C and holding at that temperature for several hours to several tens of hours according to the prior method, it is hearth cooled, air cooled or quenched, or slowly cooled temporarily to 550°C or less, and then again held for several hours to several tens of hours at 900-1000°C, followed by hearth cooling, air cooling, or quenching. Examples of the chemical composition of Co-based heat resistant alloy used in the present invention are presented in Table 1. In Table 1, entries marked with o are necessary constituents ordinarily included in Co-based alloys. In addition to the elements listed in this table, it will also include elements such as silicon, sulphur, phosphorus, nitrogen, manganese and/or copper, ordinarily included as impurities in Co-based heat resistant alloys.

Table 1

| Constituent | Range | Constituent | Range | Constituent | Range |
|--------------|-----------|-------------|--------|-------------|--------|
| o Chromium | 10-35% | Zirconium | 0-1.0% | Niobium | 0-5% |
| o Nickel | 0-30% | o Boron | 0-1.0% | Tantalum | 0-10% |
| o Tungsten | 0-25% | o Iron | 0-8% | Yttrium | 0-1.0% |
| o Molybdenum | 0-10% | Titanium | 0-2% | Co | rest |
| o Carbon | 0.01-1.0% | Aluminium | 0-2% | | |

When carrying out chromizing treatment on Co-based heat resistant alloys, making the chromizing treatment holding for 3-15 hours at 1050-1200°C offers the following effects.

- (a) An adequate chromizing treatment layer is obtained.
 - (b) Precipitates in the Co-based heat resistant alloy (various types of carbide, nitride and intermetallic compound) are partly removed, and with holding for at least 3 hours at at least 1050°C, they are almost completely dissolved, so that the alloy becomes uniform.
 - (c) Since there is no need to carry out solution heat treatment by using a furnace with non-oxidizing atmosphere after chromizing treatment, as in the prior art, it is possible to save heat energy and time, and it is economic.
- In aforementioned Co-based heat resistant alloys, high temperature strength depends on solid solution strengthening and precipitation with various precipitates. The former, solid solution strengthening is fully expressed because, as mentioned in (b), due to treatment at 1050-1200°C for 3-15 hours the alloy forms a uniform solid solution. Then, as for the latter, precipitation hardening, because the alloy is cooled from a temperature of 1050-1200°C and then prior ageing treatment is carried out at a temperature of no more than 1000°C, adequate precipitation of precipitates occurs. Therefore, adequate mechanical properties are obtained.

It should be noted that the metal structure is stable, because a solid solution is formed at ca. 1050-1200°C for 3-15 hr, and aged at a temperature of no more than 1000°C.

5 Examples

(1) An alloy A having the chemical composition shown in Table 2 was treated by the treatment of the present invention or the prior treatment shown in Table 3, and then a creep and shear test and ordinary temperature shear test were carried out.

As the results in Table 4 show, the creep and shear properties and tensile properties of the material treated by the treatment in the present invention did not fall short of those of the material submitted to the conventional treatment.

Therefore, the treatment of the present invention offers economy in terms of heat energy and time, because it is possible to omit solution heat treatment (holding at 1149°C for 4 hours).

Table 2. Chemical composition of the alloy

| Alloy | C | Cr | Ni | W | Fe | B | Co |
|---------|------|------|-----|-----|-----|-------|-----------|
| Alloy A | 0.25 | 30.5 | 9.5 | 7.2 | 3.4 | 0.007 | remainder |

Table 3. Alloy A chromizing and heat treatment conditions

| Type | Chromizing and heat treatment conditions |
|-----------------------------|--|
| Treatment of this invention | (1) Chromizing (holding for 10 hr at 1100°C, then slow cooling (ca. 1.5°C/min)) (2) Ageing treatment* (holding for 10 hr at 927°C, then hearth cooling to 538°C and air cooling) |
| Prior treatment | (1) Chromizing (holding for 10 hr at 1100°C, then slow cooling (ca. 1.5°C/min)) (2) Solution heat treatment* (3) Ageing treatment* (holding for 4 hr at 1149°C, hearth cooling to 927°C, holding at 927°C for 10 hr, then hearth cooling to 538°C and air cooling) |

* In a non-oxidizing atmosphere (argon gas)

Table 4. Alloy A treatment conditions and mechanical properties

| Type | Creep-shear test* | | | Tensile properties | | | |
|------|-------------------|-----------|--------|--------------------------------|-------------------------------------|-----------|--------|
| | Shear time | Stretch % | Draw % | 0.2% stress kg/mm ² | Tensile strength kg/mm ² | Stretch % | Draw % |
| This | 34.9 | 36.2 | 48 | 48.4 | 68.7 | 9.0 | 9.5 |

| | | | | | | | |
|-----------|------|------|----|------|------|------|------|
| invention | 35.1 | 43.4 | 48 | 49.6 | 71.1 | 10.0 | 12.7 |
| Prior | 34.1 | 36.4 | 38 | 53.0 | 75.9 | 14.2 | 15.9 |
| treatment | 38.7 | 42.8 | 45 | 56.8 | 76.2 | 10.0 | 15.9 |

* Experimental conditions: temperature 816°C
stress 17.6 kg/mm²

(2) An alloy B having the chemical composition shown in Table 5 was treated by the treatment of the present invention or the prior treatment shown in Table 6, and then creep and shear tests and cross-section microstructure tests were carried out.

As the results presented in Table 7 show, the creep and shear properties of the material subjected to treatment of this invention did not fall short of those of the material submitted to the conventional treatment. in addition, as shown in Plate 1, cross-section microstructure showed good chromizing treatment layer and microstructure.

Table 5

| Alloy | C | Cr | Ni | W | Fe | B | Co |
|---------|------|------|------|-----|------|-------|-----------|
| Alloy B | 0.20 | 24.9 | 11.0 | 7.9 | 0.45 | 0.006 | remainder |

Table 6. Alloy B chromizing and heat treatment conditions

| Type | Chromizing and heat treatment conditions |
|-----------------------------|---|
| Treatment of this invention | (1) Chromizing (holding for 10 hr at 1120°C, then slow cooling (ca. 1.5°C/min)) (2) Ageing treatment* (holding for 4 hr at 982°C, then hearth cooling to 538°C and air cooling) |
| Prior treatment | (1) Chromizing (holding for 10 hr at 1100°C, then slow cooling (ca. 1.5°C/min)) (2) Solution heat treatment* (3) Ageing treatment* (holding for 4 hr at 1149°C, hearth cooling to 982°C, holding at 982°C for 4 hr, then hearth cooling to 538°C and air cooling) |

* In a non-oxidizing atmosphere (argon gas)

Table 7. Alloy B treatment conditions and mechanical properties

| Type | Creep and shear properties* | | |
|-----------------------------|-----------------------------|-----------|--------|
| | Shear time | Stretch % | Draw % |
| Treatment of this invention | 87.0 | 49.0 | 40 |
| | 80.4 | 23.5 | 37 |
| Prior treatment | 81.5 | 27.7 | 32 |
| | 90.5 | 29.6 | 38 |

*Experimental conditions:
Temperature 816°C
stress 17.6 kg/mm².

(3) Table 8 shows the results of high-temperature corrosion tests on alloy A having the chemical composition in Table 2 after being treated by the treatment of the present invention or the prior treatment shown in Table 3. As is clear from the results, it is evident that resistance to high temperature corrosion is also nearly unchanged from the prior product.

Table 8. High temperature corrosion test

| | |
|-----------------------------|--|
| Experimental conditions | 900°C, 50 hours, buried in Na ₂ SO ₄ , under 0.3% SO ₂ gas |
| Prior treatment | 10.5 mg/cm ² |
| Treatment of this invention | 11.1 mg/cm ² |

4. Simplified Description of the Drawings

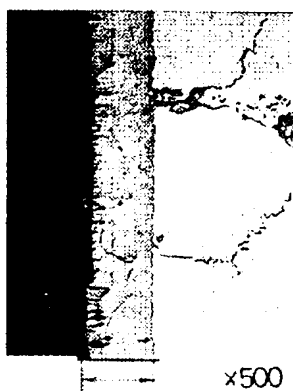
Figure 1 is a photograph showing the surface microstructure of alloy B obtained with the treatment of the present invention.

Figure 2 is a photograph showing the internal microstructure of alloy B obtained with the treatment of the present invention.

Agent Akira Uchida
Agent Ryoichi Hagiwara

Plate 1

Plate 2



Cr: chromizing treatment layer

Amendments

27 August 1976

- 5 Commissioner, Patent Office Ishiro Katayama
1. Designation of the Case
1976 Japanese Patent Application No. 22224
- 10 2. Title of the invention
Method for treating a cobalt-based heat resistant alloy
3. Amending party
15 Involvement Applicant
Address 1-5-2 Marunouchi, Chiyoda-ku, Tokyo-to
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- 5 Date of the Order to Amend voluntary amendment
6. Number of inventions added by the amendment None
30
7. Subject to Amendment
(1) Specification, claims
(2) Specification, detailed description of the
invention
35
8. Content of Amendment
(1) The claims are amended as per the separate sheet.

- (2) Specification, column 3, line 13, amend "Zr: 0-10%" to "Zr: 0-1.0%".

Claims

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Method for treating a cobalt-based heat resistant alloy characterized in that a cobalt-based heat resistant alloy comprising, in wt%, Cr: 10-35%, Ni: 0-30%, W: 0-25%, Mo: 0-10%, C: 0.01-1.0%, Zr: 0-1.0%, B: 10 0-1.0%, Fe: 0-8%, Ti: 0-2%, Al: 0-2%, Nb: 0-5%, Ta: 0-10%, Y: 0-1.0%, Co: remainder, is subjected to chromizing with simultaneous solution treatment of the alloy at 1050-1200°C, and then subjected to ageing treatment at no more than 1000°C.

Translator's Report/Comments

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Your order of (date): 21/12/2011

In translating the above text we have noted the following apparent errors/unclear passages:

| Page/para/line* | Comment |
|---|--|
| Claims line 3 + column 3 line 13 | Zr: 1-10% should be Zr: 1-1.0% (see "amendments" section) Errors corrected and underlined in translation for ease of reference. |

* This identification refers to the source text. Please note that the first paragraph is taken to be, where relevant, the end portion of a paragraph starting on the preceding page. Where the paragraph is stated, the line number relates to the particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.